A Study on Mechanochemical Decomposition of Chlorinated Organic Compounds and Wastes(有機塩素化合物とそれを含有する廃棄物のメカノケミカル分解に関する研究)

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論文内容要旨

There have been numerous chlorinated organic compounds developed these days, and some of them exhibit toxicity when they are exposed in the environment. In addition, even if the non-toxic polymer compounds containing chlorine in their structures are subjected to heating, it may be possible to create toxic chlorinated organic compounds such as dioxins. Of course, these chlorinated organic compounds have shown excellent chemical and physical properties, and are useful materials, but once they are disposed, they should be decomposed by a proper method.

There have been several methods for decomposing the chlorinated organic compounds. Although these current methods are effective in dechlorination and decomposition, each exhibits certain technological and economical drawbacks. Recently, much attention has been paid to the mechanochemical treatment of toxic substances, because of its easy operation and reliability for decomposing the compounds. The mechanochemical phenomena can be demonstrated by grinding, and it is known that grinding plays a significant role in causing mechanochemical effects on solid particles as well as in reducing particle size (Figure 1). One of the unique phenomena of this effect is to dissociate the material by rupturing the bonds. And chemical reactions to form new compounds occur in some cases. It has been noted that such reaction can be applied to the treatment of decomposition of chlorinated compound, namely, into inorganic chloride. However, little information about the dechlorination mechanism during the mechanochemical treatment of the compounds has been available.

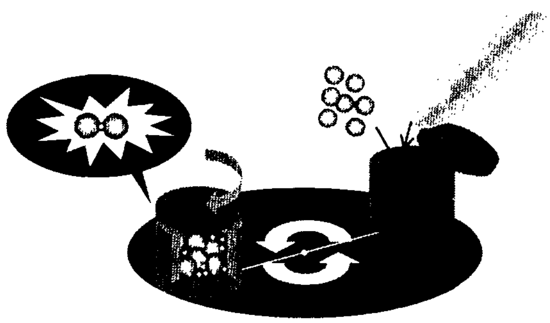

Figure 1 Planetary ball mill.

This represents the purpose of this thesis, which deals with the novel method for decomposing toxic chlorinated organic compounds by means of mechanochemical treatment. Furthermore, this treatment has been applied to the decomposition of waste of commercial products, which contain chlorinated organic compounds.

The 1st chapter of this thesis considers this proposal against the background of the strong demand for decomposing chlorinated organic compounds, and surveys the previous work after which it explains the purpose of this study. The chlorinated organic compounds dealt with in this work are dioxins, PCBs and the like, and examples of the decomposition by using current decomposition methods are shown. This chapter also offers a simple explanation of mechanochemistry, which is utilized as the experimental method in this thesis.

The 2nd chapter deals with the decomposition of trichlorobenzenes (TCB); 1,2,3- and 1,3,5- TCB as chlorinated organic compound samples. The sample was ground with calcium oxide (CaO) powder in air by using a planetary ball mill. The grinding has induced mechanochemical reaction between the two compounds, resulting in the decomposition of TCB through dechlorination from the benzene nucleus. The mechanochemical dechlorination was monitored by analytical methods as follows: X-ray diffraction (XRD), thermogravimetry (TG), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, electron resonance (ESR), gas chromatography/mass spectrometry (GC/MS) and ion chromatography (IC), respectively. Experimental results showed that the remaining amount of TCB decreased with the increase in grinding time, and reached almost 0% at 360 min. In addition, the water-soluble amount of chloride increases correspondingly and reached about 95%, indicating the successful transformation from organic chloride into inorganic one (Figure 2). Additionally, the other final products detected after grinding were carbon and some minor methane and ethane, although the formation of some chlorine-containing intermediate phases such as dichlorobenzene and tetrachlorobenzene was observed in the early stage of grinding (for 1 h). Radicals were generated during the decomposition process, predominantly due to the rupture of C–Cl bonds in the molecule. Although various intermediate phases were formed to indicate the complexity of the decomposition, a possible decomposition was dechlorination. Consequently, TCB, as an example of chlorinated, can be decomposed by dry grinding with CaO transforming organic compounds into inorganic products. In addition, computer chemistry work was performed to clarify the decomposition mechanism. Simulation data revealed that the C–Cl bond was the weakest bond in the TCB and TCB decomposition would be caused by dechlorination, and this is well agreement with the experimental result.

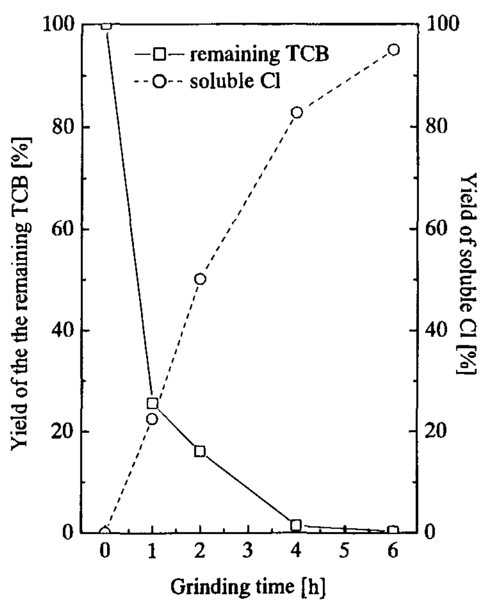

Figure 2 Change in the yield of the remaining TCB and water-soluble Cl with grinding time. Grinding condition is as follows: TCB:CaO=1:12 molar ratio, 700 rpm.

The 3rd chapter deals with the decomposition of *monochlorobiphenyl* (BP-Cl) as a *polychlorinated biphenyl* (PCB) model sample by cogrinding with different additives such as metal oxides and hydroxides. Mechanochemically induced dechlorination of BP-Cl on the surface of metal oxide was compared with that on metal hydroxide, using three metals of Mg, Al, and La. The metal oxides, such as γ-alumina, magnesium oxide, and lanthanum oxide were found to demonstrate efficient ability to dechlorinate the BP-Cl, which was, however, remained in the ground samples when all the corresponding hydroxides were used. According to the results of electron spin resonance (ESR) and GC/MS analyses, the formation of radicals due to effective charge

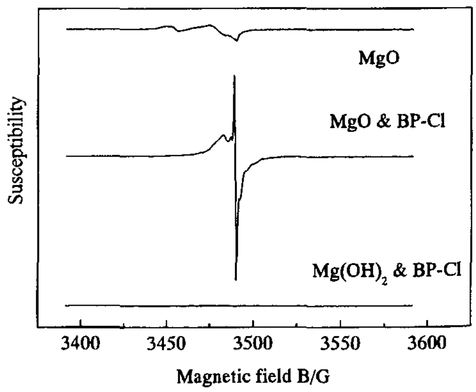

Figure 3 ESR spectra of the 6 h ground samples of MgO and $Mg(OH)_2$ with 5% BP-Cl mixture and MgO 6 h ground sample.

transfer played a significant role to decompose the chlorinated organic compounds, when the oxide was used as additive. On the other hand, no decomposition of BP-Cl was well consistent with the absence of radicals in the case of hydroxides used (Figure 3). The role of inorganic additives on the decomposition efficiency is basically interpreted in terms of the surface reaction initiated by the mechanochemically induced charge transfer from the reductive O^{2-} site rather than the metal site in the inorganic additives. This decomposition process would originate in the charge separation on oxygen of inorganic additives, and, subsequently, it would be induced charge transfer from oxygen to organic compound. This process generates radicals, which fill the important role of this reaction. These data indicated the following advice: decreasing sample moisture and using hard additives such as quartz during the grinding, to effectively induce charge transfer within the ground samples.

The 4th chapter deals with new reactants, which can decompose effectively monochlorobiphenyl (BP-Cl) by the grinding. CaO is one of good additives for the decomposition of chlorinated organic compounds mechanochemically, however, it takes a long time to accomplish this purpose. Cogrinding of BP-Cl sample with one of the rare earth oxides was conducted in ambient air using the planetary ball mill to investigate the mechanochemical decomposition performance. Cogrinding with the rare earth oxide could decompose the BP-Cl sample. Comparing with the previous experiments using CaO, MgO, and Al_2O_3 as additive, the efficiency of degradation of BP-Cl on the rare earth oxide has been enhanced and the time required to decompose the BP-Cl sample becomes short. Although the process of decomposition is complex, in general, rare earth oxide such as La_2O_3, Gd_2O_3, Nd_2O_3, Y_2O_3, indicated an excellent performance in decomposition of BP-Cl by the grinding.

The 5th chapter deals with the decomposition of practical product wastes, which contain chlorinated organic compounds, such as aromatic polyamide so-called aramid. A film sample of aramid was subjected to grinding in air with CaO powder by using the planetary ball mill, to investigate its mechanochemical decomposition. The reaction was accelerated with an increase in the grinding time, and all chlorine in the film sample was transformed into inorganic chlorides in prolonged grinding. The main products after decomposition reaction were water-soluble calcium chloride hydrate, amorphous carbon, calcium carbonate, and a small amount of calcium nitrite, as a result of a rupture in the covalent bonds of C–C, C–Cl, C–N, and C–H in the aramid film construction into new bonding (Figure 4). The most significant phenomenon was the formation of $Ca(NO_2)_2$, suggesting the strong oxidative ability of CaO during the mechanochemical reaction.

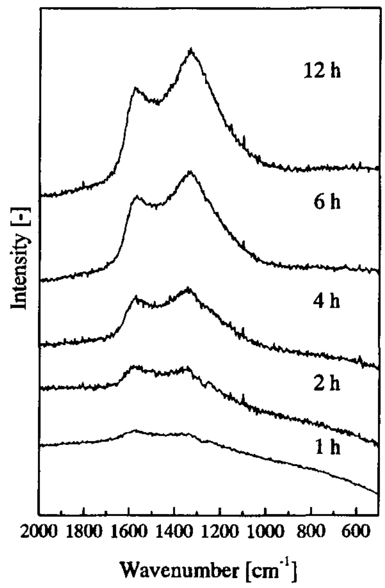

Figure 4 Raman spectra of the aromatic amide film and CaO mixed ground samples with different grinding time.

The 6th chapter deals with the decomposition of magnetic recording tapes with dechlorination and their recycling. Evaporation tape has been treated to recover the contained cobalt (Co) metal with dechlorination by dry grinding the tape only or cogrinding with CaO, respectively. The induced mechanochemical reaction between Co and chlorine in the tape leads to the formation of cobalt chloride ($CoCl_2$), which is water-soluble, offering a novel process to recover the metal from the tape. On the other hand, cogrinding the tape with CaO allows the complete transformation of chlorine in the tape into water-soluble inorganic chloride. Nitrous anion and fluorine ion are detected in the filtrate from the washing with water, confirming that the added CaO exhibits the strong oxidizing ability to form the organic composition as well as the absorption of chlorine. A series of mechanochemical treatment and washing operations was applied to extracting Co from the ground magnetic tapes.

The 7th chapter is the summary of the present thesis, which is composed of the conclusions obtained in each chapter. In this thesis, a novel decomposition method has been proposed and its applicability for the waste of commercial products has been investigated in this work. In any cases, further investigation would be need. However, due to the decomposition of chlorinated organic compounds and their products, the mechanochemical method using metal oxide or rare earth oxide is very effective. As a result, it is confirmed that this reaction is deeply related with the radical formation and decomposition reaction of these are dechlorination. Therefore, it can be summarized that the mechanochemical decomposition against chlorinated organic compounds would be useful and effective method.

論文審査結果の要旨

有害有機塩素化合物が多く破棄される状況にあり、環境汚染が危惧されている。工場跡地などでも、長い間放置された器具から PCB などが漏れ出し、土壌や油などに混入して希薄な状態ながらも汚染が広まる事態が少なくない。一方、磁気テープなどの磁気記録媒体も塩素を樹脂相に含むが、役目を終えたテープ製品は廃棄物となり、多くは焼却や埋め立て処分される。このとき、適切な塩素回収設備や燃焼温度管理下にない焼却施設では、有害な塩素ガスやダイオキシン類などが環境を汚染する危惧がある。これには、焼却以前に適切に処理できる方法の開発が望まれる。もちろん、幾つかの処理法が提案されている中、焼却法や化学的触媒法でない、より環境に優しい処理法として、メカノケミカル(MC)法が注目されている。この方法では、確実に有機有害物が無害化できるが、その反応機構が必ずしも解明されているとはいえず、より効率良い MC 処理条件を見出す上では無害化機構の解明と、多くの事例が必要であり、確実に目的が達成されていることを確認することが重要である。

本論文は、遊星ミルを無害化処理装置として用い、有害有機物としてテトラクロロベンゼン(TCB)、モノクロロビフェニル（BP-Cl）の試薬と、有機塩素化合物を含む２種類の廃棄物を用い、また、これに添加する物質として CaO を始め、幾つかの金属酸化物を選択し、MC 処理後の有機相ならびに塩素基の挙動と結合状態を中心に評価し、有害有機物の無害化機構解明を中心に検討し、これを明確にした研究内容であり、全編７章よりなる。

第１章は序論である。

第２章は、1, 2, 3-TCB ならびに 1, 3, 5-TCB を対象とし、これに CaO を添加して空気中で粉砕（MC）処理し、TCB-CaO 間での MC 反応を X 線回折法や FT-IR 法などを駆使して評価している。その結果、TCB 構造中の C-Cl 結合は、処理時間とともに変化し、無機 Ca 塩化物となることを明確にしている。その反応機構は、脱塩素反応であることを確認した。更に、MC 処理時間に対する脱塩素率は、はじめは徐々に、やがて急激に変化し、最後はそのスピードが遅くなって平衡に達することを定量的に表示している。これによって、TCB－CaO 系の MC 処理では、ポリ塩化ビニル（PVC）で確認されるような脱塩化水素反応とは異なる機構で進行することを明らかにしている。

第３章ならびに４章は、BP-Cl を対象物質とし、まず、３章では、Mg、Al、La の金属酸化物ならびにそれらの水酸化物を添加材として選択して遊星ミル処理した場合の BP-C l の脱塩素挙動を観察評価し、その反応機構解明を行った。その結果、BP-Cl の MC 脱塩素には、酸化物が有効であること、その場合、ラジカルが発生すること、発生ラジカルは比較的長い生存時間を持つことが判明した。このことは、BP-Cl の MC 脱塩素反応を期待するには、水酸化物添加は効果がないこと、また、酸化物添加の場合も MC 処理雰囲気を乾燥状態とすることが重要であるなど、実用化する上での有用な情報を提示している。一方、４章では、金属酸化物として希土類酸化物を添加剤とした場合、最も優れた添加剤は La 酸化物であることを明確にし、その場合の反応機構を解明している。

第５章ならびに６章は、２種類の有機塩素化合物を含有する廃棄物の MC 処理による脱塩素が主目的であるが、同時に、それに含有する金属有価物（主として Co）回収が可能か否かの検討も行っている。添加剤としては、最も典型的な CaO を用いたが、それでも脱塩素がスムーズに進行することを確認し、その脱塩素機構を明確にしている。一方、磁気テープに含有する Co はテープそのものと固相反応し、$CoCl_2$ が生成することを確認し、それが水溶性であることから水抽出・ろ過によって回収できることを明確にした。このときの CaO は MC 処理時の酸化反応を促進させる役割を果たすことを確認している。

第７章は結論である。

以上、要するに本論文は、有害有機塩素化合物ならびに有機塩素化合物を含有する製品などの廃棄物の非加熱による処理と有価物回収のための MC 処理における操作条件に対する指針を示したものであり、地球工学、素材工学の発展に寄与するところ少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。